

(MWNT) cathodes as a function of the voltage applied. The average field strength at  $10 \mu\text{A}/\text{cm}^2$  was  $4.32 \text{ V}/\mu\text{m}$ .

EXAMPLE 15.

The DWNT material produced according to EXAMPLE 1 were crushed and mixed with pastes, slurried and screen printed on stainless steel plate and dried in air at  $500^\circ\text{C}$  to produce a CRT cathode. This cathode material was tested according to EXAMPLE 13. The average field strength at  $10 \mu\text{A}/\text{cm}^2$  was  $1.54 \text{ V}/\mu\text{m}$  with very uniform electron emission.

**What is claimed is:**

1. A method of producing fullerenes comprising double walled nanotubes (DWNTs), which comprises providing a source of carbon and a catalyst comprised essentially of transition metal of the iron group of the periodic table of the elements and sulfur, in a reaction zone having a DWNT forming atmosphere comprised essentially of hydrogen containing gas, subjecting said carbon and catalyst to heat in the reaction zone, thereby to produce hot carbon containing vapor, quenching the hot vapor in said DWNT forming atmosphere thus condensing the hot vapor, collecting the resulting product and recovering said DWNTs from the resulting product outside the heated region of the reaction zone.
2. The method of claim 1, wherein the DWNT forming atmosphere contains an inert gas in addition to a hydrogen containing gas.
3. The method of claim 1, wherein the pressure of said DWNT forming atmosphere is in the range of 10 Torr to 3 atmospheres.
4. The method of claim 2, wherein the pressure of said DWNT forming atmosphere is in the range of 10 Torr to 3 atmospheres.
5. The method of claim 3, wherein the pressure of said DWNT forming atmosphere is about one half of ambient atmosphere.
6. The method of claim 4, wherein the pressure of said DWNT forming atmosphere is about one half of ambient atmosphere.

7. The method of claim 2, wherein the DWNT forming atmosphere is comprised essentially of a mixture of elemental hydrogen and argon gases.
8. The method of claim 3, wherein the DWNT forming atmosphere is comprised essentially of a mixture of elemental hydrogen and argon gases.
9. The method of claim 7, wherein the hydrogen and argon gases are present in a molecular ratio of hydrogen to argon equal to 0.1-2.0
10. The method of claim 8, wherein the hydrogen and argon gases is present in a molecular ratio of 3 hydrogen to 5 argon.
11. The method of claim 1, wherein the catalyst is comprised essentially of a mixture of iron, cobalt and nickel with sulfur.
12. The method of claim 2, wherein the catalyst is comprised essentially of a mixture of iron, cobalt and nickel with sulfur.
13. The method of claim 1, wherein the catalyst is comprised essentially of a mixture of iron, cobalt and nickel with sulfur.
14. The method of claim 7, wherein the catalyst is comprised essentially of a mixture of iron, cobalt and nickel with sulfur.
15. The method of claim 8, wherein the catalyst is comprised essentially of a mixture of iron, cobalt and nickel with sulfur.
16. The method of claim 11, wherein the catalyst mixture is comprised of 27% iron, 14% cobalt, 51% nickel and 8% sulfur, by weight.
17. The method of claim 12, wherein the catalyst mixture is comprised of 27% iron, 14% cobalt, 51% nickel and 8% sulfur, by weight.
18. The method of claim 13, wherein the catalyst mixture is comprised of 27% iron, 14% cobalt, 51% nickel and 8% sulfur, by weight.
19. The method of claim 14, wherein the catalyst mixture is comprised of 27% iron, 14% cobalt, 51% nickel and 8% sulfur, by weight.
20. The method of claim 15, wherein the catalyst mixture is comprised of 27% iron, 14% cobalt, 51% nickel and 8% sulfur, by weight.
21. The method of claim 5, wherein the carbon is provided as a consumable carbon electrode of an arc discharge electrode system that provides the heat in the reaction zone and wherein the catalyst mixture is contained within the consumable electrode.

22. The method of claim 18, wherein the carbon is provided as a consumable carbon electrode of an arc discharge electrode system that provides the heat in the reaction zone and wherein the catalyst mixture is contained within the consumable electrode.
23. The method of claim 19, wherein the carbon is provided as a consumable carbon electrode of an arc discharge electrode system that provides the heat in the reaction zone and wherein the catalyst mixture is contained within the consumable electrode.
24. The method of claim 20, wherein the carbon is provided as a consumable carbon electrode of an arc discharge electrode system that provides the heat in the reaction zone and wherein the catalyst mixture is contained within the consumable electrode.
25. The method of claim 21, wherein the consumable electrode is a carbon rod having the catalyst mixture contained in a central core thereof.
26. The method of claim 22, wherein the consumable electrode is a carbon rod having the catalyst mixture contained in a central core thereof.
27. The method of claim 23, wherein the consumable electrode is a carbon rod having the catalyst mixture contained in a central core thereof.
28. The method of claim 24, wherein the consumable electrode is a carbon rod having the catalyst mixture contained in a central core thereof.
29. The method of claim 21, wherein the consumable electrode is comprised of carbon particles and particles of the catalyst material in a compacted mixture.
30. The method of claim 22, wherein the consumable electrode is comprised of carbon particles and particles of the catalyst material in a compacted mixture.
31. The method of claim 23, wherein the consumable electrode is comprised of carbon particles and particles of the catalyst material in a compacted mixture.
32. The method of claim 24, wherein the consumable electrode is comprised of carbon particles and particles of the catalyst material in a compacted mixture.
33. The method of claim 1, wherein the sulfur of the catalyst is present as a sulfide of at least one of the metals, iron, cobalt and nickel.
34. The method of claim 2, wherein the sulfur of the catalyst is present as a sulfide of at least one of the metals, iron, cobalt and nickel.
35. The method of claim 11, wherein the sulfur of the catalyst is present as a sulfide of at least one of the metals, iron, cobalt and nickel.

36. The method of claim 12, wherein the sulfur of the catalyst is present as a sulfide of at least one of the metals, iron, cobalt and nickel.
37. The method of claim 1, wherein the catalyst is subjected to the preliminary step of heating a mixture of particles of iron, cobalt, nickel and sulfur under temperature conditions suitable to cause a reaction of sulfur with the other metals of the mixture, thereby producing metal sulfides.
38. The method of claim 2, wherein the catalyst is subjected to the preliminary step of heating a mixture of particles of iron, cobalt, nickel and sulfur under temperature conditions suitable to cause a reaction of sulfur with the other metals of the mixture, thereby producing metal sulfides.
39. The method of claim 26, wherein the catalyst is subjected to the preliminary step of heating a mixture of particles of iron, cobalt, nickel and sulfur under temperature conditions suitable to cause a reaction of sulfur with the other metals of the mixture, thereby producing metal sulfides.
40. The method of claim 23, wherein the catalyst is subjected to the preliminary step of heating a mixture of particles of iron, cobalt, nickel and sulfur under temperature conditions suitable to cause a reaction of sulfur with the other metals of the mixture, thereby producing metal sulfides.
41. The method of claim 35, wherein the catalyst is subjected to the preliminary step of heating a mixture of particles of iron, cobalt, nickel and sulfur under temperature conditions suitable to cause a reaction of sulfur with the other metals of the mixture, thereby producing metal sulfides.
42. The method of claim 1, wherein the catalyst is present as a mixture of particles of the metals and sulfur comprising the catalyst.
43. The method of claim 2, wherein the catalyst is present as a mixture of particles of the metals and sulfur comprising the catalyst.
44. The method of claim 42 wherein the mixture of particles comprising the catalyst is present within a hole provided in the core of a carbon electrode comprising a source of the carbon to be vaporized and wherein said electrode is the anode of an electric arc discharge that serves to subject said carbon to heat for vaporization thereof.
45. The method of claim 42, wherein the carbon to be heated for vaporization in the reaction zone is present as particles of carbon mixed with the mixture of particles comprising the catalyst particles.
46. The method of claim 45 wherein the mixture of carbon particles and catalyst particles is consolidated to form the anode electrode of an electric arc discharge system that serves to subject said compacted mixture to the heat for vaporization thereof.

47. The method of claim 45 wherein the mixture of carbon particles and catalyst particles is present within a hole provided in the carbon electrode which also serves as a source of the carbon to be vaporized and wherein said electrode is the anode of an electric arc discharge that serves to subject said carbon to heat for vaporization thereof.
48. The method of claim 11, wherein the sulfur of the catalyst is present as elementary sulfur.
49. The method of claim 12, wherein the sulfur of the catalyst is present as elementary sulfur
50. The method of claim 1, wherein the hydrogen containing gas of the DWNT forming atmosphere is comprised essentially of one or more of hydrogen gas, and hydrocarbon gas selected from among methane, ethane, and acetylene.
51. The method of claim 2, wherein the hydrogen containing gas of the DWNT forming atmosphere is comprised essentially of one or more of hydrogen gas, and hydrocarbon gas selected from among methane, ethane, and acetylene.
52. The method of claim 21, wherein alternating current is used to maintain the arc discharge of the electrode system.
53. The method of claim 52, wherein the carbon is provided as a pair of electrodes each having holes containing the catalyst mixture and both of which are consumed during the arc process.
54. The method of claim 53, wherein at least one electrode is rotated during the arc operation.
55. The method of claim 21, wherein the flow of initial gas mixture through the reactor is maintained during the arc operation.
56. The method of claim 52, wherein the flow of initial gas mixture through the reactor is maintained during the arc operation.
57. The method of claim 21, wherein the initial gas mixture is maintained without being substituted during the arc operation.
58. The method of claim 52, wherein the initial gas mixture is maintained without being substituted during the arc operation.
59. The method of claim 1, wherein the initial gas mixture is pyrolyzed by thermal heating to 1200-1400°C over the said catalyst.
60. The method of claim 7, wherein at least one of the gases chosen from among thiophene vapor, hydrogen sulfide, carbon disulfide and benzene vapor is added to the initial gas mixture.

61. The method of claim 60, wherein the gas mixture is pyrolyzed over the supported metal catalyst, prepared by regeneration of a catalyst that is active in DWNT synthesis performed in the arc discharge system.
62. The method of claim 61, wherein the supported metal catalyst is prepared by, first, burning off the carbon out of the product of DWNT synthesis in the arc, second, dispersing the remainder in a liquid to form a slurry, third, applying the slurry to the surface of an inert support, preferably aluminum nitride, forth, reducing metal oxides to the metal state in a hydrogen containing atmosphere at elevated temperature.
63. The method of claim 60, wherein the gas mixture is pyrolyzed over the supported metal catalyst, prepared by impregnation-drying-calcination-reduction technique, using for impregnation the combined solution of iron, cobalt and nickel salts, taken in molar ratio about 2:1:4, correspondingly.
64. The method of claim 60, wherein the gas mixture is pyrolyzed over the floating catalyst obtained by delivering into the gas flow the benzene solution of iron, cobalt, nickel and sulfur compounds, chosen from among metallocenes and carbonyls of Fe, Co, and Ni, and from among thiophene and carbon disulfide, correspondingly.
65. The method of claim 61, wherein catalytic pyrolysis is accomplished by inductively coupled high frequency plasma in a flow-through tubular reactor at reduced pressure, employed instead of thermal heating of gas flow.
66. The method of claim 62, wherein the catalyst is comprised of a mixture of particles of iron cobalt nickel and sulfur that is subjected to the preliminary step of heating under temperature conditions suitable to cause a reaction between the sulfur and the other metals of the mixture thereby producing sulfides of said metals and wherein the powder comprising said catalyst is dispersed in the influent gas and thus delivered into plasma region of vertically installed tubular reactor.
- ~~67.~~ A solid substance composed by more than one half by weight of hollow carbon nanotubes having walls consisting essentially of two layers of carbon atoms.
- ~~68.~~ An electron-emissive material comprising a surface consisting primarily of a plurality of emissive tubules wherein each of the plurality of emissive tubules is generally nanotubes with a controlled number of graphene layers.

69. The electron-emissive material of claim 68, wherein the number of the graphene layers is two (2).
70. The electron-emissive material of claim 68, wherein the electron-emissive material is composed of a mixture of double wall and few walls (less than 5 wall) nanotubes.
71. The electron-emissive material of claim 69, wherein an overall composition of the electron-emissive material comprises of at least 20% double walled nanotubes.
72. The electron-emissive material of claim 69, wherein an overall composition of the electron-emissive material comprises of at least 70% of double walled nanotubes.
73. The electron-emissive material of claim 70, wherein an overall composition of the electron-emissive material comprises at least 20% of few walled (less than 5 wall) nanotubes.
74. The electron-emissive material of claim 70, wherein an overall composition of the electron-emissive material comprises up to 90% of mixed walled nanotubes.
75. The electron-emissive material of claim 68, wherein each of cylindrical layers of the nanotubes having a lattice spacing of 0.35 – 0.45 nm.
76. The electron-emissive material of claim 69, wherein end cap of the double wall nanotubes with double layer curvature which generates greater electric field strength than a single curvature, graphitic sheet, edge or ridge emitter.
77. The electron-emissive materials of claim 76, wherein the curvature of the double wall nanotubes and sharpened end elements curvature is within the range of 1.7 -5.5 nm.
78. The electron-emissive material of claim 69, wherein the double wall nanotubes have a diameter is greater than 1.2 nm.
79. The electron-emissive material of claim 78, wherein majority of the double wall nanotubes with diameter in the range of 2.7 nm to 5.5 nm.
80. The electron-emissive materials of claim 69, wherein the double wall nanotubes have length greater than 1000 nm.
81. The electron-emissive material of claim 69, wherein a plurality of the double wall nanotubes are oriented to cause electric field enhancement.
82. The electron-emissive materials of claim 69, wherein the double wall nanotubes emit electron at an average electric field of less than 10 V/ $\mu$ m.
83. The electron-emissive materials of claim 82, wherein the double wall nanotubes are characterized by the emission of electrons at an average electric field of less than 5V/ $\mu$ m.

84. The electron emissive materials of claim 82, wherein the double wall nanotubes are characterized by the cold emission of electrons at an average electric field of less than  $2\text{V}/\mu\text{m}$ .

85. A field emission device comprising:

A cathode having an electron-emissive material, the electron-emissive material having a surface consisting of a plurality of nanotubes with a controlled number of graphene layers uniformly distributed over the surface, wherein each of the plurality of emissive element is generally a double walled nanotubes, and an anode disposed to receive electrons emitted from the electron-emissive cathode.

86. A field emission device as defined in claim 85, comprising a vacuum chamber for enclosing said cathode and anode.

87. A field emission device as defined in claim 86, comprising a control grid interposed between the cathode and anode in controlling the electron flow from the cathode to the anode in response to an electric bias voltage applied to the control grid relative to the cathode.

88. A field emission device as defined in claim 87, wherein the fluorescent light emitting element positioned to receive electrons emitted from the cathode.

89. A field emission device as defined in claim 89, comprising a CRT, wherein the anode, cathode and control grid are adapted and arranged to have electric voltage applied thereto for causing the cathode to emit electrons in response to an applied control grid voltage for controlling the light emitted by the fluorescent elements as a function of the applied grid voltage.

90. Fullerene material comprising double walled carbon nanotubes produced by the method of claim 1.

91. Fullerene material comprising double walled carbon nanotubes produced by the method of claim 2.

92. Fullerene material comprising double walled carbon nanotubes produced by the method of claim 3.



